

# SCIENCE FOR GLASS PRODUCTION

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## COLLOIDAL COLORING OF GLASSES: UNRECOGNIZED NANOTECHNOLOGIES (review)

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Work on colloidal coloring of glass by metallic and nonmetallic nanoparticles is reviewed. The particulars of the technology and the character of glass coloring are shown. The experimental and practical results obtained are discussed from the standpoint of nanotechnologies.

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**Key words:** colloidal coloring, nanocrystals (metallic, nonmetallic), color setting, colorants, nanotechnology.

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Many materials and processes which mankind has used for a long time are actually created by means of unrecognized nanotechnologies. Accidentally created and subsequently discovered nanoobjects and nanoprocesses are traditionally used in existing technologies, especially those associated with disperse systems.

Colloidal chemistry is concerned with the laws and physical-chemical phenomena occurring in disperse (colloidal) systems. Practically all substances and materials encountered in daily life are objects of colloidal chemistry [1]. As this line of work advances, more specialized disciplines branch out from it. For example, the physical chemistry of polymers and the physical chemistry of surfaces started to develop at the end of the 1950s and supramolecular chemistry at the end of the 1970s [2–4]. These directions are directly associated with the development of nanotechnologies [5].

The chemistry and technology of glass (micro-nonuniform structure of glass, production of sitals, opacification and colloidal coloring of glass, sol-gel technology, and others) are no exceptions. A characteristic example is the coloring of glass by colloidal nanoparticles of metals, a process known since ancient times [6]. However, information on glass compositions and technologies for fabricating articles has not been preserved; the work was revived only in the 17th century by A. Kassii and J. Kunckel [7]. In his book *On Gold* (1685) A. Kassii gave the first description of a method for obtaining and using a red dye consisting of gold and tin

compounds, which was later named “Kassii’s purple pigment.” Glass made with this colorant was colorless on cooling, but reheating produced a red color. J. Kunckel developed a commercial method for producing golden ruby glass.

Colloid-colored glasses include glasses whose color is due to metallic and nonmetallic nanocrystals. Gold, silver, and copper are metals while cadmium sulfoselenide ( $\text{CdS} \cdot n\text{CdSe}$ ), cadmium sulfide ( $\text{CdS}$ ), antimony sulfide ( $\text{Sb}_2\text{S}_3$ ), and other compounds are nonmetals that produce colloid coloring in glass.

Colloidal coloring of glass advanced in the second half of the 20th century in connection with the adoption of continuous production of heat-polished sheet glass and the production of photosensitive glass and sital.

Methods for producing nanoobjects and the properties and applications of nanoobjects in glass technology are reviewed in [8–10].

### COLOR OF COLLOIDAL SYSTEMS

The color of colloidal systems is determined by their phase and, correspondingly, optical nonuniformity. Optical properties such as light absorption and scattering are most characteristic for these systems [1, 8].

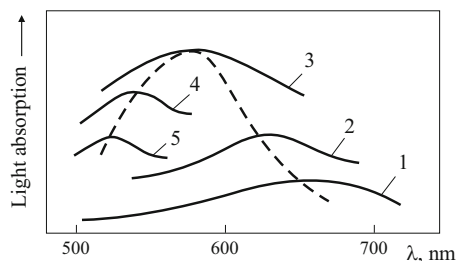
Light transmission (absorption) by homogeneous media is determined by the Bouguer–Lambert–Beer law

$$I = I_0 e^{-Kl} = 10^{-kl}, \quad (1)$$

where  $I$  is the intensity of the light flux which has passed through the sample or layer of solution;  $I_0$  is the initial inten-

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**Fig. 1.** Light absorption by gold sol versus the wavelength of the incident light and dispersity of the sol (the dispersity increases in the order of the numbers on the curves).

sity of the light flux;  $l$  is the path length of the light flux (thickness of the sample or layer of solution);  $K$  is the natural index of refraction;  $k$  is the decimal absorption coefficient ( $k = 0.434K$ ); for colored glasses the degree of light absorption is directly proportional to the colorant concentration  $c$  and the coefficient  $\varepsilon$  characterizing the specific absorption of the colorant ( $k = \varepsilon c$ ).

For a disperse (colloidal) system it is evident that the particle size of the disperse phase does not appear in the Bouguer–Lambert–Beer equation. One would think that the dispersity of colloidal systems should not influence their capability to transmit (absorb) light. However, the effect of the size colloidal particles on light transmission (absorption) is indirect, occurring via light scattering. The point is that a portion of the radiation (mainly short wavelength) of transmitted white light is lost because of light scattering, and this loss will be perceived as absorption. In contrast to true absorption, when light energy is absorbed by the system and is converted into heat, the absorption due to light scattering is said to be fictitious. In this case the Bouguer–Lambert–Beer equation takes the form

$$I = I_0 e^{-(K+K')l}, \quad (2)$$

where  $K'$  is the coefficient of fictitious absorption.

Since opalescence depends on the particle size,  $K' = f(r)$ , where  $r$  is particle radius.

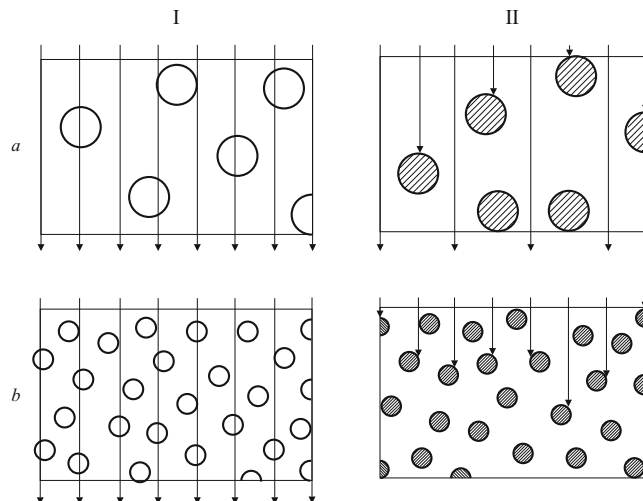
If  $K = 0$ , i.e., if the sol is white, Eq. (2) taking account of the fictitious absorption will have the form

$$I = I_0 e^{-K'l} = I_0 \exp [-(K'l/\lambda^4)], \quad (3)$$

since according to Rayleigh's equation light scattering is inversely proportional to the fourth power of the wavelength  $\lambda^4$ .

For fictitious absorption the color of the sol will be different in transmitted and scattered light. In both cases it is not the proper color of the sol material but rather it is due to opalescence.

In respect to absorption as well as light scattering, metallic sols exhibit anomalous behavior as compared with other colloidal systems. Just like opalescence, absorption by metallic sols reaches a maximum value at a certain wavelength



**Fig. 2.** Diagram showing the change of screening with increasing dispersity of nonmetallic (I) and metallic (II) sols: a) low-dispersity sols; b) high-dispersity sols with the same content of the disperse phase.

and a certain particle size. Figure 1 shows the dependence of light absorption by gold sol versus the wavelength of the incident light and the dispersity of the sol. It is evident that as the sol dispersity increases, the maximum absorption of light shifts toward short wavelengths, and initially the magnitude of this maximum increases and then decreases.

The existence of a maximum is partially explained by the fictitious absorption, which for metallic sols reaches a maximum at some average dispersity. However, opalescence is insufficient to cause such a sharp effect. The sharp increase of light absorption with increasing dispersity is explained by the considerable capability of the metallic particles to absorb and scatter light. Under such conditions, for the same concentration of the disperse phase the more highly disperse metallic particles will screen light better.

This situation can be understood from the diagrams I and II in Fig. 2. The diagram I shows the passage of light rays through a nonmetallic sol with transparent particles. In this case it makes no difference whether the disperse phase will be in a sol in the form of large or small particles; because the sol is transparent light passes through either system. The diagram II shows the passage of light rays through a metallic sol. Even very small metallic particles can block the passage of light. Since the degree of screening will increase with the dispersity, stronger light absorption will occur.

Thus, for a metallic sol the Bouguer–Lambert–Beer law must take account of the dispersity  $r$ :

$$I = I_0 \exp \{ -[Kl/f(r^3)] \}. \quad (4)$$

As the dispersity increases further the particles of the metallic sol become so small that they no longer serve as an obstacle for light transmission. In this case a sol will behave as a true solution.

M. Faraday (1857) performed the first fundamental studies of the color of colloidal solutions. He showed convincingly that the red color of gold sols is due to ultramicroscopic metallic particles of gold.

Natural and artificial colloidal systems are very often colored. The color of precious or semiprecious stones is often due to the presence in them of small amounts of metals and their oxides in the colloidal state [11, 12]. Metal sols possess a very bright color. This is explained by the large difference of the densities and refraction coefficients of the disperse phase and dispersion medium.

As noted above, the color of metallic sols is due to the true absorption and scattering of light by metallic particles. Since absorption and scattering pass through maxima with increasing particle size and light wavelength, sols of the same metal can show the most diverse colors. For example, comparatively coarsely disperse gold hydrosols with comparatively weak true absorption, which is shifted to the red side of the spectrum, and strongly scattering light with a maximum in the same part of the spectrum have, ordinarily, a blue or light blue color (in transmitted light) and opalesce with a red color (in scattered light). Conversely, highly disperse gold sols are, ordinarily, red and opalesce with a light blue color. This is explained by their ability to absorb strongly light with a sharp maximum in the yellow-green part of the spectrum. Light scattering by red gold sols is very weak because of the high dispersity of the sols, and it has no effect on the color. Gold sols with still higher dispersity become yellow and approach the ion-molecular color of gold chloride solutions.

In many cases the question of the color of metallic sols is made more complex by the fact that aside from the dispersity of a system the particle shape and structure affect light absorption and scattering.

## FOUNDATIONS OF NANOTECHNOLOGIES

The concept of nanotechnologies (NT) as a possibility of creating materials and structures with prescribed properties by means of controlled assembly from individual atoms was first formulated by the American physicist R. Feynman in 1961 [13].

As yet the term “nanotechnology” does not have a single, universally accepted definition. At the present time the following definition has been adopted at the State Corporation Rusnanotech: “*nanotechnology is a collection of technological methods and techniques used to study, design, and produce materials, facilities, and systems, including targeted monitoring and control of construction, chemical composition, and interaction of the components of their individual nanoscale elements (size of the order of 100 nm and less in at least one dimension), which lead to the improvement or appearance of additional operational and/or user characteristics and properties of the products obtained.*”

The objects of nanotechnologies can be directly low-dimensional objects with dimensions characteristic for the nanorange as well as macroscopic objects (bulk materials, individual elements of devices and systems), whose structure is controllably created and modified with resolution at the level of individual nanoelements. Facilities or systems are considered to be made using nanotechnologies if at least one of their basic components is a nanotechnology object, i.e., there exists at least one stage of the technological process whose result is a nanotechnology object [14].

Nanosize systems in accordance with their intermediate position between the world of atoms and molecules and the world of microscopic and macroscopic bodies can be obtained in two basic ways:

by dispersion, i.e., comminution (grinding) of large bodies following the principle *top down*;

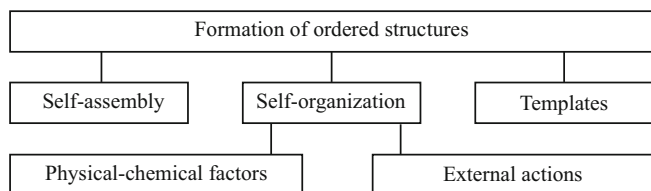
by condensation, i.e., formation of nanoparticles (aggregates) from individual atoms and molecules following the principle *bottom up*; it should be noted that nanostructured systems obtained by condensation methods (“bottom up”) are more stable than the systems created by means of dispersion (“top down”).

For the production of a number of materials with properties determined by nanoparticles, the formation of new structures usually occurs as a result of so-called “self-processes.” The concepts *self-organization* and *self-assembly* were introduced into supramolecular chemistry by Lehn in the course of a study of the spontaneous formation of inorganic complexes [4]. According to Lehn self-organization and self-assembly describe two different but partially overlapping classes of phenomena, self-assembly being a broader term than self-organization.

Essentially, these concepts came to supramolecular chemistry from biochemistry, where they already occupied an important place earlier, since biosynthesis can occur only as a result of “self-processes.” In supramolecular chemistry, “self-processes” touch only the super-molecular level with noncovalent bonds. At the same time these processes can also serve as characteristics of physical-chemical processes with covalent bonds, for example, crystallization processes. For nanoparticles of metals, it is customary to study ensembles of the particles themselves and the protective layers formed. Special attention must be given to the influence of the chemical nature of these layers on self-organization and self-assembly processes.

At the present time there are no adequately clear definitions of these phenomena and assessments of their applicability to different processes, but many studies along different lines and for different materials have confirmed the fruitfulness of such an approach to nanotechnologies. Generalizing the data from a number of works [4, 15, 16], “self-processes” can be briefly characterized as follows:

– *self-organization is an ordering process occurring in an open system as a result of matched interaction of many constituent elements; in physics and chemistry self-organiza-*



**Fig. 3.** Diagram of the formation of ordered structures during the implementation of nanotechnologies.

tion is a transition from disordered motion of atoms and molecules to ordered structures;

– *self-assembly is the process of formation of an ordered structure or medium, such that the components (elements) of the initial structure, additively comprising or “assembling” as parts of a whole and realize a complex structure, participate in the process in a practically unchanged form*; in a number of technological processes self-assembly can start after the appropriate self-organization.

A diagram showing the formation of ordered structures during the implementation of nanotechnologies is displayed in Fig. 3.

It follows from the diagram that the self-organization of particles in the system usually occurs as a response of a system to an external action. The character of this action is directly related with the chemical composition and properties of the constituent substances of the system. Self-organization can be used just as a mechanism for creating complex templates, processes and structures at a higher hierarchical level of organization compared with the initial level. This mechanism is realized as a result of numerous and multivariant interactions at low levels (atoms, molecules) where the interactions occur according to local laws, different from the collective laws governing the behavior of the self-ordering system itself.

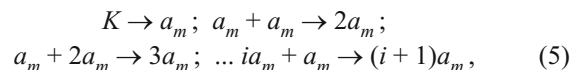
Self-assembly of ordered structures can occur under the influence of gravitational, electric, and magnetic fields as well as surface forces and other factors.

We shall briefly examine the role of “self-processes” during volume crystallization of substances, which plays a substantial role in a number of technological processes, including in glass production. The mechanism of volume crystallization of substances is best described by the cluster model, proposed by H. S. Frank and W. Y. Wen (1957) and generalized in [17–19]. According to this model, during volume crystallization in metastable systems (supercooled or supersaturated), before a stably growing new phase appears, intense generation of nanoclusters of crystallizing matter occurs. Numerous data obtained by electron-microscopy, IR-spectroscopy, and other methods have confirmed the presence of such cluster formations. Typical cluster sizes are 2–8 nm.

A classical example of the cluster model for molecular liquids is water. Liquid water is a conglomerate of large associates (clusters) of  $H_2O$  molecules which appear and once

again decay. The idea of an “ice-like” structure of such flickering clusters is based on x-ray and infrared studies, which have shown that the arrangement of water molecules inside clusters is similar to their arrangement in the crystal lattice of ice; as temperature decreases, the number of molecules in a cluster increases. So, the average number of molecules in a cluster is 15–50 at 65°C and 90–120 at 0°C. Thus, according to the cluster model ice-like formations exist in water even before the first stable ice crystals form [18].

An analytical model of the crystallization of substances taking account of the formation of nanoclusters in a supersaturated phase and the appearance and growth of embryos of crystals by attachment of nanoclusters is proposed in [19]. Stable nanoclusters form as a result of successive interactions between monomers (atoms or molecules) and subsequently between clusters of the dissolved substance. The clusters are quite mobile. They can diffuse in the matrix and unite with one another forming embryos of a new phase — crystals. These embryos are spheroidal particles, often nanoclusters. Since the supersaturated (supercooled) phase consists of monomers and nanoclusters, in general crystal growth occurs by means of nanoclusters and monomers. However, at high initial levels of metastability the elementary acts change changing the size of crystal embryos are absorption and emission of nanoclusters by them. Here the bicluster interactions proceed according to the scheme



where  $K$  is the source of nanoclusters;  $a_m$  is a single cluster;  $2a_m$  and  $3a_m$  are crystal-like formations, embryos, formed when two or three clusters coalesce;  $i a_m$  are embryos and nanocrystals formed from  $i$  clusters; for high supersaturation (supercooling) and concentration of clusters larger than in an equilibrium solution the reverse decomposition reactions in the scheme (5) are slow and can be neglected.

The cluster mechanism of growth by this scheme is characteristic for rapid growth of crystals from comparatively uniform melt, for example, at high initial supercooling (or supersaturation) or for slow growth under conditions of marked micrononuniform melt structure and high viscosity, which is characteristic for glass-forming melts. Clusters have a large effect on the crystallization process, leading to excitation of auto-oscillatory structures. On the whole it is shown in [19] that self-maintaining coupled oscillations of the intersection of crystallized matter, density of nanoclusters, and distribution functions of solid-phase particles can appear in nanocluster systems.

Generalizing what has been said above, it should be noted that self-organization of the kinetic units of a liquid (water, solution, melt) in crystal-like aggregates from which embryos form and then crystals form (self-assembly) owing to attachment of individual nanoblocks occurs under the influence of external actions.



A characteristic example of self-assembly is the formation of natural precious opal, which consists of small, transparent, spherical particles of amorphous silica of approximately the same size (about 200 nm), closely packed in a regular order. These spheres are in contact with one another and the intervals between them are filled with air, water vapor, or water. An investigation of the structure of precious opal showed that the spherical particles of opal are formed by concentric shells, comprised of silica nanospheres (20 – 50 nm) [12]. These nanospheres appear during very slow evaporation of water (possibly, over hundreds and thousands of years) and with increasing silica concentration in a hydrothermal solution. Under the conditions of natural hydrothermal synthesis under the action of gravity and surface forces there formed a fractal structure which is thermodynamically most favorable and can occur spontaneous by means of self-assembly [12, 20]. The constantly accumulating knowledge concerning the structure of opal and the development of a theory of its formation in nature have made it possible to synthesize this mineral artificially (1964).

At the present time synthetic opal matrices are ordinarily formed by sedimentation, and due to the presence of a photonic band gap (PBG) their optical properties are the same as those of semiconductors. During synthesis the self-organization and self-assembly processes result in the creation of a closely packed nanoporous structure. Filling the nanopores with particles of ferromagnetic material, for example, nickel, it is possible to obtain a nanocomposite used in microwave filters.

## COLLOIDAL COLORING OF GLASSES

As noted above, glasses whose color is due to metallic (gold, silver, and copper) and nonmetallic (cadmium and antimony sulfides and sulfoselenides, and others) nanocrystalline formations are colloiddally colored glasses.

Metals belong to the first secondary subgroup of D. I. Mendeleev's periodic system and therefore have similar physical-chemical properties. All three methods of this subgroup are distinguished by low chemical activity, specifically, they bond with oxygen with great difficulty; for this reason their oxides reduce easily to metals. On the basis of chemical activity these metals can be placed in sequence Cu – Ag – Au. Gold and silver do not bind with atmospheric oxygen directly, while their oxides obtained via other paths easily decompose, forming pure metal and oxygen. Copper bonds more easily with oxygen; the comparatively stable oxides  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  are known for it. Above  $800^\circ\text{C}$  the copper oxide (II) begins to decompose in accordance with the reaction equation  $2\text{CuO} = \text{Cu}_2\text{O} + \text{SO}_2$ . On heating gold and silver oxides start to decompose at about  $200^\circ\text{C}$ . Accordingly, to obtain colloiddally colored copper glasses the glassmaking conditions be reducing; glass colored with silver can be made under reducing as well as oxidizing conditions, since even under neutral conditions gold can be re-

duced to metal and precipitate in the form of droplets. Therefore, the solubility of these metals in molten glass likewise decreases in the progression Cu – Ag – Au. This is confirmed in [7, 21 – 24].

The melting temperatures of these metals are lower than the usual formation temperatures of glass articles. In this connection, they can crystallize only in the formation interval; in practice, it starts below these temperatures, since the nanosize effect of a decrease of the melting and crystallization temperatures starts to have an effect [14].

The most common color due to colloidal nonmetallic compounds is due to the formation of sulfides, selenides, and sulfoselenides of metals in the second transition (Cd) and sixth main (S, Se) subgroups of the periodic system (compounds of the type  $\text{A}^2\text{B}^6$ ). Cadmium sulfides and selenides have similar crystal lattices, crystallize in a hexagonal system, and give the compounds  $\text{CdS} \cdot n\text{CdSe}$ , which form a continuous series of solid solutions (mixed crystals), which are responsible for glass color from yellow to brown.

In silicate melts, including in glasses, diffusion processes are slow and, for sufficiently fast cooling, there is not have enough time for them to go to completion. For this reason, when minerals are formed in nature nonuniform crystals with zonal structure, i.e., the interior and exterior layers have different chemical composition, are formed. Equilibrium is not reached for such systems; they are fixed in a metastable state. Similar phenomena are also observed in glasses colored by cadmium sulfoselenides (selenium rubies). Selenium ruby is a traditional name, but it is conventional, since it does not reflect the essence of the red color imparted by cadmium sulfoselenides to glasses. In this case the color of the glass is determined by the ratio of the amounts of CdS and CdSe in the glass and changes from yellow (CdS) to red (with increasing CdSe). The color of the glass is determined mainly by the color of the disperse phase, which possesses pronounced transmission; the effect of the particle size is weaker. Some questions of the physical chemistry and technology of glasses colored by colloidal nonmetallic compounds, specifically, cadmium sulfoselenides, have been examined in [25].

Generalizing this information, it should be noted that self-organization of colorant units into crystal-like aggregates occurs as a result of external action; embryos are formed from these aggregates and individual nanoblocks bond together to form crystals (self-assembly).

Ordinarily, the color of glass is obtained after "setting," i.e., soaking the articles in definite temperature intervals to grow the colorant particles. Good-quality gold ruby should be purple – red; sometimes special techniques are used to shift this color either into the violet or red end of the spectrum. Silver gives a yellow color. Copper ruby glass has a dark-red color. Technological questions concerning the production of colored glass, including colloidal-colored glass, are illuminated in [7, 21 – 25]. The particulars of the formation of nanocrystals are similar to those for sitals [26, 27].

The chemical activity of metals in the first secondary group of the periodic system, including with respect to oxygen (especially, for Ag and Au), and their comparatively low solubility in molten glass had been noticed before. Thus, on the basis of the cluster model it can be asserted that at glassmaking temperatures these metals in the glass melt are in the atomic and ionic states with atomic clusters, continually being formed and decaying, predominating. For a more active metal, an elevated amount of the ions  $\text{Cu}^+$  can be present in the melt together with atomic clusters [24].

We shall now examine from the standpoint of nanotechnology the processes involved in the formation of ordered structures in glasses containing the above-mentioned metallic and nonmetallic particles.

**Self-Organization.** Self-organization phenomena start after the main glassmaking steps have been completed. Even though the temperature of the glass melt is high, equilibrium in the system of ions of the forming and decaying atomic clusters of metals becomes more stable, i.e., the melt adapts to the new conditions. In this case, in accordance with the scheme shown in Fig. 3, energy (temperature) and physical-chemical (glass composition) factors play the main role.

Many investigators have examined the theoretical foundations of crystallization processes including its initial stages [26–28]. On the basis of thermodynamic conditions, the work of formation of a critical embryo of new phase  $A_c$  is given by

$$A_c = B\sigma^3/(\Delta c)^2, \quad (6)$$

where  $\sigma$  is the interphase tension at the boundary of the initial (solution, melt) and new phases;  $\Delta c$  is the supersaturation (the supercooling parameter  $\Delta T$  can also be used for crystallization); and,  $B$  is a constant associated with the physical constants of matter.

It follows from Eq. (6) that of decisive significance for the magnitude of the work of formation of critical embryos of a new phase is the interphase tension at the boundary separating the phases during the formation of the separation surface. In addition, the greater the supersaturation (supercooling), the higher the formation probability of an embryo and the smaller its size are.

In this connection, soluble additives introduced in relative small quantity and capable of changing the value of  $A_c$  can have a large effect on the embryo formation process. This effect can be positive or negative. In the first case the interphase tension at the boundary separating the initial phase from the new phase decreases and the degree of supersaturation (supercooling) for which critical embryos of the new phase form also decreases. In the second case the additive inhibits interparticle exchange on the interphase boundary and appears to block the surface of the nucleating phase. Small additions can also displace the boundary of metastability from the region of high supersaturation (supercooling) into the region of small values of these parameters, thereby creating favorable conditions for conducting the corresponding technological processes, for example, crystallization.

It is noted in [26] that in application to ceramic systems it is more convenient to characterize the effect of small additions by the concepts of modification, since they encompass not only acceleration (sensitization, mineralization) but also retardation (inhibition, stabilization) of the process. But, for glasses the concepts “modification” and “modifiers” have a different meaning and characterize oxides, ions, or processes that weaken the cohesion of the silicon-oxygen network. In this connection, the narrower concept “modifiers of colloidal coloring” (MCC) should be used in application to colloidal coloring of glass.

Tin compounds are used as MCC to obtain colloiddally colored glass. These compounds are also used as thermal and chemical sensitizers in light-sensitive glasses; when silver coats glass surfaces in glass production, tin and lead compounds are used as sensitizers ( $\text{SnCl}_2$ ) and surface activators ( $\text{PbCl}_2$ ) [29]; tin compounds are used as catalysts in the production of sitals [26, 27]. The main purpose of MCC in coloring is to ensure an adequate volume concentration and formation rate of crystallization centers with relatively slow rate of crystal growth. The role of tin compounds in obtaining glass colored with metallic nanocrystals will be examined in greater detail below.

Thus, for colloidal coloring of glass the composition of the glass and the temperature conditions determine the self-organization of the metal atoms in the glass right up to the formation of embryos of the crystals (centers of crystallization).

**Self-Assembly.** Crystal embryos up to 10 nm in size formed in the process of self-organization do not give rise to color in glass; in addition, a rapid increase of the viscosity during the formation of glass articles results in a rapid retardation of transport phenomena (diffusion) and “freezing” of the high-temperature structural state together with the crystal embryos. In order for color to appear additional heat-treatment of the glass (“setting”) is necessary; during this process the finished glass articles are held at a definite elevated temperature. In the process the viscosity of the glass decreases, transport phenomena are activated, and conditions are created for growth of nanocrystals on the embryos formed. Under prescribed conditions the crystallization process proceeds spontaneously and can be regarded as a self-assembly process. The required rate of the process is obtained by choosing the appropriate temperature and by the presence of MCC in the glass. Ordinarily, tin compounds are used for MCC and play a stabilizing role at this stage. The process of crystal growth has been studied quite well and is described in the specialized literature, specifically, in [26, 27].

## COMPOSITIONS OF GLASSES, TECHNOLOGY, SPECTRAL CHARACTERISTICS

The compositions of colloiddally colored glasses are given in Table 1. Other compositions are also used; they are systematized in [21–23]. These works also examine the

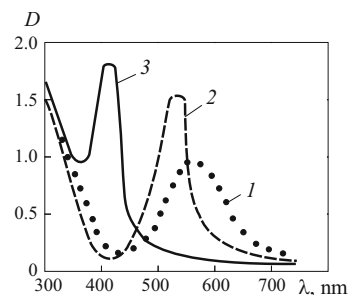
technological particulars of glass making, production, “setting,” and the spectral characteristics.

It should be noted that gold and copper ruby glasses are now used comparatively rarely, mainly for making high-art objects. Yellow silver glasses are extremely rarely used, and the technologically more adaptable and less expensive glasses colored with CdS are used instead. Silver and copper are also used with stain coloring (cementation) for photosensitive glasses; in this case the color carriers are also nanoparticles of metals [7, 21–24]. Yellow and red glasses colored by CdS and CdS · nCdSe are most widely used for decorative and technical purposes.

**Coloring of Glass by Metallic Nanocrystals.** This form of glass coloring is used to make decorative-artistic and technical articles. Coloring in this case is similar that of the corresponding colloidal solutions, which was examined above, and is due to the absorption and scattering of light by metallic nanocrystals, precipitated during the shaping and heat-treatment of glass articles.

*Colloidal coloring of glasses for decorative-artistic articles.* The carriers of the color characteristic for each metal in glasses are 10–60 nm particles of metal. To obtain the optimal color for the glass the sizes of the metal nanocrystals must have a narrower range. For example, for gold ruby of good quality the size of the gold nanocrystals must be in the range 20–40 nm. Corresponding tones appear above and below this interval: below 20 nm—yellow and above 40 nm—violet. For nanocrystal sizes above 60 nm glass acquires a blue color. Similar sizes of metallic nanocrystals, optimizing the color, are also characteristic for other types of glass colored with colloidal metals. It should be noted that the ranges indicated here are approximate, since nanocrystals of other sizes will unavoidably be present in the glass. In addition, together with the sizes of nanocrystals their volume concentration must also be taken into account; it is determined by the composition of the glass and the conditions of glassmaking, production, and “setting.”

Figure 4 shows spectral absorption curves of glasses whose colors are due to gold, silver, and copper nanocrystals [30]. Comparatively narrow wavelength sections bounded by absorption maxima characterize the presence of optimal particle sizes for a given color. The broadening of the absorption bands at the bottom of the spectral curves attests to the pre-



**Fig. 4.** Absorption spectra of glasses colored by colloidal metals: 1) copper; 2) gold; 3) silver.

sence of nanocrystalline formation of other sizes; in addition, for copper rubies, together with Cu<sup>0</sup> nanocrystals, Cu<sup>+</sup> can also have coloring effect [24].

It was noted above that self-organization of the coloring elements in glass is determined by the composition of the glass and the temperature conditions. The glass compositions and the temperature regimes of glassmaking, production, and heat-treatment for colloiddally colored glass were determined and perfected over a long period of time. For example, the optimal compositions of gold and copper rubies, the temperature regimes of glassmaking, and the production of articles and “setting” were first found and perfected in the 17th century.

It was established that the most beautiful tones and the most intense coloring of gold rubies are obtained in lead-silicate glasses. Low-lead and lead-free glass compositions can also be used but for quite intense and reproducible coloration tin compounds must be added to them. The solubility of gold and other colloidal-coloring metals also increase with temperature, so that comparatively high temperatures must be used to make these glasses. Gold rubies require an oxidizing regime; other colloiddally colored glasses are not so sensitive to the redox conditions, though copper rubies require moderately reducing conditions for glassmaking with reducing agents introduced into the mix without fail.

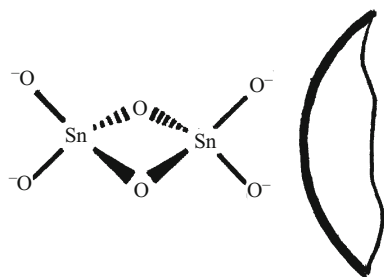
As noted above, for glasses colored by metallic nanocrystals tin compounds, which are colloidal coloring modifiers (MCC), must be introduced without fail. At high temperatures tin is present in the molten glass predominately in the form Sn<sup>2+</sup> and is a metallophilic agent, which increases the

**TABLE 1.** Compositions of Colloiddally Colored Glasses (Content, wt.%)

Glass type	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	PbO	CaO	ZnO	Na <sub>2</sub> O	K <sub>2</sub> O	As <sub>2</sub> O <sub>3</sub>	Sb <sub>2</sub> O <sub>3</sub>	SnO <sub>2</sub>	Colorants*
Gold ruby (purple-red)	52.2	2.8	29.0	—	—	1.0	13.5	0.5	0.5	0.5	Au — 0.05
Silver (yellow)	72.0	0.5	—	8.0	—	9.9	9.0	—	—	0.6	Ag — 0.06
Copper ruby** (red)	75.4	—	—	7.0	—	17.6	—	—	—	0.6	Cu <sub>2</sub> O — 0.5
Selenium ruby (red)	68.0	3.0	—	—	12.0	12.0	5.0	—	—	—	CdS — 1.7 Se — 1.9

\* Colorants are added in amounts above 100%.

\*\* Reducing agents are introduced into the mix.



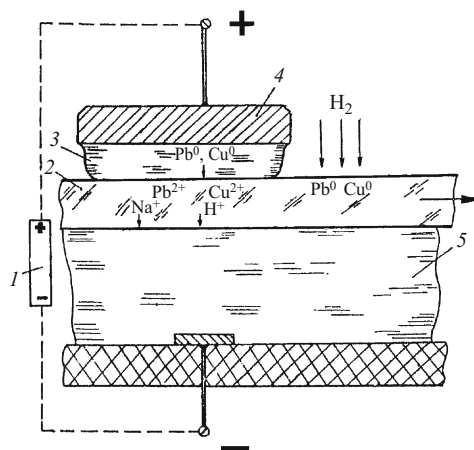
**Fig. 5.** Diagram of the mutual arrangement of nanocrystals of metals and tin-oxygen anions.

solubility of metals (Au, Ag, Cu) in the molten glass. This is necessary to obtain on cooling a sufficiently large quantity of crystallization centers; the rate of growth of the crystals must be low. If these conditions are not satisfied, the glass does not become colored during setting, the ruby color is formed with difficulty, and the glass easily acquires a brown (liver) tone.

The composition and technological particulars of obtaining colloiddally colored glasses is described in [21–23]. W. Weyl has made the most detailed analysis of the role of tin compounds during the formation of ruby color and silver staining of glass surfaces [7].

It is well known that lead and tin compounds at sufficiently high content in glass are capable of forming in the glasses their own extended formations similar to silicon-oxygen, but with low forces constants [31, 32]. A comparatively low content of tin compounds in colloiddally colored glasses results in the formation of individual tin-oxygen anions. When the glass is cooled, a restructuring of the oxygen compounds of tin occurs with the transformation  $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+}$  and partial polymerization (individual complex ions  $\text{Sn}_2\text{O}_6^{4-}$  are formed). These ions are formed near atomic clusters of metals and this process promotes the appearance of an interphase surface of spheroidal embryos of crystals (centers of crystallization) of the metals under study. After an interfacial surface appears, the tin-oxygen anions increase the interphase tension and impede interparticle exchange on the interphase boundary, slowing the rate of subsequent crystal growth. A possible relative arrangement of the  $\text{Sn}_2\text{O}_6^{4-}$  around spheroidal nanocrystals of metals (Au, Ag, Cu) in glasses is presented in Fig. 5. A similar arrangement of metals and complex anions is also observed in nature with the formation of spheroidal nanocrystals of native gold, matrix-stabilized in silicate and sulfide tin- and lead-containing rock [33].

Certain particulars of obtaining copper ruby glasses, which are characterized by an unstable reproducibility of the red color and are prone to form dark tones, should be noted. There are other opinions concerning the nature of the color of these glasses. For example, the results of experiments and calculations concerning the color carriers in copper ruby glasses are presented in [24]. Low-melting glasses of the sys-



**Fig. 6.** Diagram of continuous surface coloring of float-glass.

tem  $\text{Na}_2\text{O}$  and  $\text{B}_2\text{O}_3$  (30%  $\text{Na}_2\text{O}$  and 79%  $\text{B}_2\text{O}_3$ ) were used; the reduction conditions were created by means of an external source of  $\text{H}_2$  and evaluated according to the oxygen partial pressure. It is shown that  $\text{Cu}^0$  and  $\text{Cu}^+$  are found in the copper ruby glasses obtained; the author's opinion is that it is precisely  $\text{Cu}_2\text{O}$  that plays the determining role in the formation of ruby color.

*Continuous colloiddal coloring of float-glass.* This form of coloring is obtained by the electrochemical method in a thin surface layer of the glass: low-melting metals and alloys are used for coloring [34].

A diagram of the apparatus for electrochemical coloring of a glass surface is shown in Fig. 6. The melt of coloring metal must wet the holding electrode well and not wet the glass strip. When using an alloy consisting of 98–99% lead and 1–2% copper, the holding electrode is made of copper. The tin melt is the cathode, lead-copper melt the anode, and the glass strip the electrolyte. The holding electrode keeps the lead-copper melt constantly in contact with the glass strip over its entire length. When the glass strip 2 is in contact with the coloring metal melt 3 (from above), held in place by the holding electrode 4, and with tin melt 5 (from below) an electrochemical cell operating in the electrolysis regime is formed when a constant voltage is applied from the source 1. Ionization of the lead and copper ions occurs under the electric field at the anode – glass boundary:  $\text{Pb}^0 \rightarrow \text{Pb}^{2+} + 2e$ ,  $\text{Cu}^0 \rightarrow \text{Cu}^+ + e$ . The lead and copper ions diffuse into the surface layer of the glass, while the sodium and hydrogen ions diffuse into the tin. As a result of the high viscosity of the glass and short time of its contact with the coloring melt, the penetration of the lead and copper into the glass is limited to a thin surface layer. After the glass strip exits the electrochemical contact zone the hydrogen of the protective atmosphere diffuses into the glass and is ionized:  $1.5\text{H}_2 \rightarrow 3\text{H}^+ + 3e$  and reduces the lead and copper ions:  $\text{Pb}^{2+} + 2e + 2\text{H}^+ \rightarrow \text{Pb}^0 + 2\text{H}^+$  and  $\text{Cu}^+ + e + \text{H}^+ \rightarrow \text{Cu}^0 + \text{H}^+$ . In the process,



nanoparticles of metals are formed and colloidal coloring of the glass occurs.

A layer of colored glass is up to 20  $\mu\text{m}$  thick, and most of the metallic particles of size about 40 nm are concentrated in a about 1  $\mu\text{m}$  thick layer. A reduced layer of metals directly on the glass surface evaporates at high temperatures; a surface microlayer of colorless glass is protective in this case, increasing the operational reliability of the sheet glass.

Similar phenomena occur during heat treatment of articles made of  $\text{K}_2\text{O} - \text{PbO} - \text{SiO}_2$  glasses in a reducing flame [8]. The glass acquires color ranging from grey to black. An oxidizing flame can remove this color.

**Coloring in light-sensitive glasses.** The light sensitivity of the glasses is determined by the fact that the coloring complexes or nanoparticles of certain metals, located in glass, can under the influence of an energetic or a chemical activation process (irradiation, sensitization, heat-treatment) change the color or form crystal embryos capable of further growth and formation of nanocrystals [7, 8, 23, 24].

Photosensitive additives are always present in photosensitive glasses. Examples of such additives are the following:

- photosensitive metals (gold, silver, copper, and others): 0.01 – 0.5%;
- optical sensitizers (usually  $\text{CeO}_2$ ), which increase the sensitivity of a metal to irradiation: to 0.05%;
- thermal sensitizers ( $\text{SbO}_3$ ,  $\text{SnO}_2$ , and others), which increase the capability of a photosensitive metal to formation of nanoparticles during heat treatment: to 0.05%.

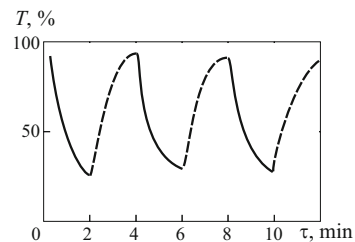
Photosensitive glass can contain one or two sensitizers. The photochemical reactions occurring in photosensitive glasses can be represented by the following scheme (according to S. Stuckey):

1) irradiation stage:  $A^x + h\nu \rightarrow A^{x+1} + e^w$  ( $A^x$  — ion of the metal  $A$ , absorbing light and having valence  $x$ ;  $h\nu$  — quantum of absorbed energy;  $e^w$  — excited photoelectron);

2) manifestation stage:  $M^y + ye^w \rightarrow (M^0)^w \rightarrow M^0 + w$  ( $M^y$  — metal ion with valence  $y$ ; for copper, silver, and gold  $y = 1$ );  $(M^0)^w$  — metal atom with excess energy supplied by a photoelectron;  $w$  — the excess energy supplied in the form of heat or light).

Many silicate compositions in which small additions of compounds of photosensitive metals are added together with sensitizers are suitable for obtaining photosensitive glasses. The purity of the initial materials must be quite high.

A distinguishing feature of photochromic glasses is a reversible change of the light transmission under cyclic exposure to the active radiation (Fig. 7). At the moment of exposure to the active radiation (ultraviolet) photochromic glass gradually becomes darker; the optical density reaches its maximum after 1–2 min after exposure to the radiation starts. After the radiation stops the transparency of the glass spontaneously returns to the initial state. Photochromism can be obtained by photolysis of halides of alkali metals ( $\text{AgCl}$ ,  $\text{CuCl}$ ) by irradiating the glass with UV radiation. The photosensitive compounds form in the glass a finely disperse



**Fig. 7.** Variation of the transmission  $T$  of photochromic glasses under cyclic exposure to activating radiation: —) darkening of glass under the action of UV radiation; ---) brightening of glass after UV irradiation.

phase (silver nanocrystals  $(\text{Ag}^0)_n$  no larger than 100 nm), uniformly distributed over the volume of the glass; photolysis of photosensitive compounds and formation of color centers occur by the scheme  $\text{Ag}^+\text{Cl}^- + h\nu \rightarrow \text{Ag}^0\text{Cl}^0$ ,  $n\text{Ag}^0 \rightarrow (\text{Ag}^0)_n$ ; after the active radiation is no longer effective, spontaneous decay of the color centers  $(\text{Ag}^0)_n$  starts with formation of the bonds  $\text{Ag}^+\text{Cl}^-$ , which is accompanied the restoration of the transparency to its initial state.

**Coloring of Glass by Nonmetallic Nanocrystals.** This form of coloring is related with the formation in glass of heavy-metal — cadmium, antimony, bismuth, and others (copper(I) oxide is possible for the obtaining ruby glasses) — sulfides, selenides, and sulfoselenides. These compounds are semiconductors and in glass they are present in the form of nanocrystalline formations not exceeding 50 nm in size. The character of the formation of nonmetallic nanocrystals is due to general laws and does not differ from those for metallic nanocrystals. At the same time there are very significant differences in the character of the interaction of light flux with the colorants.

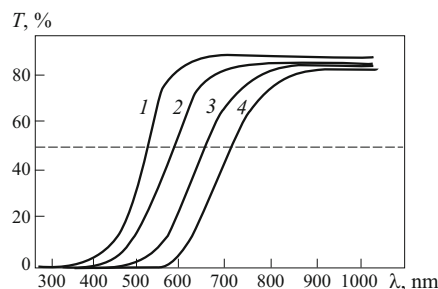
The interaction of a light flux with a colorant is associated with the presence in three bands in semiconductors: valence, conduction, and a photonic band gap (PBG) separating them. Light absorption, mainly of the high-energy short-wavelength component, results in the excitation of electrons and their transition from the valence band into the conduction band via the PBG.

For all classes of known compounds irrespective of whether or not they are in a glassy or crystalline state, the condition for transparency can be expressed by the relation

$$(hc/\lambda) < \Delta E, \quad (7)$$

where  $h$  is Planck's constant,  $c$  is speed of light,  $hc$  is the radiation quantum,  $\lambda$  is the wavelength, and  $\Delta E$  is the energy width of the bandgap of the compound.

This relation yields the limiting condition for transparency  $hc/\lambda_b = \Delta E$ , for which the energy of a photon with wavelength  $\lambda = \lambda_{\text{lim}}$  will be sufficient to excite electrons and transfer them from the valence band into the conduction band, which will be accompanied by absorption of electromagnetic radiation (light flux). It is customarily assumed that



**Fig. 8.** Transmission spectra of glasses color by cadmium sulfide (CdS) and cadmium sulfoselenide (CdS ·  $n$ CdSe): 1) CdS; 2 – 4) cadmium sulfoselenide with increasing fraction Cd ·  $n$ CdSe.

$\lambda_{\text{lim}}$  corresponds to the transmission of 50% of the incident radiation by the material (or 0.3 optical density units). For  $\lambda > \lambda_{\text{lim}}$  the material is transparent, since  $(hc/\lambda)$  is less than  $\Delta E$ ; for  $\lambda < \lambda_{\text{lim}}$  the material will be opaque, since the photon energy  $(hc/\lambda)$  is greater than the energy width of the bandgap  $\Delta E$ . Since  $h$  and  $c$  are fundamental constants, and expressing them in the appropriate units, we obtain the relation

$$\Delta E = 1237/\lambda_b. \quad (8)$$

If the band gap is known, then the transmission boundary (absorption) of the material can be determined.

The color of selenium ruby is due to the semiconducting cadmium sulfoselenides, which form a continuous series of solid solutions. The different CdS and CdSe content gives different color and tones, which is evident in the Table 2 [7, 8, 21, 25]. The data on the values of  $\Delta E$  for the coloring components are taken from the reference manual [35].

Figure 8 shows the experimental data on the spectral transmission of glass colored by cadmium sulfides and sulfoselenides [30]; the horizontal dashed line shows the 50% transmission level, from which  $\lambda_{\text{lim}}$  can be determined. This quantity can also be approximately determined from reference handbooks on PBG widths.

It has already been noted that when obtaining copper ruby glasses together with copper nanocrystals it is also pos-

sible for  $\text{Cu}_2\text{O}$  to form, which together with  $\text{Cu}^0$  is a color carrier (in nature  $\text{Cu}_2\text{O}$  is the main part of the mineral cuprite, which has a red color with different hues) [24].  $\text{Cu}_2\text{O}$  is a semiconductor with bandgap  $\Delta E = 2.0$  eV. Using the relation (8) we obtain  $\lambda_{\text{lim}} \sim 620$  nm, which corresponds to red color. Thus, taking account of the higher chemical activity of copper as compared with silver and especially gold it is entirely likely that semiconductor nanocrystals  $\text{Cu}_2\text{O}$ , which are red, are present in copper ruby glass together with metallic nanocrystals  $\text{Cu}^0$ . It is noted in [32] that since  $\text{Cu}^0$  and  $\text{Cu}^+$  are present in copper ruby glasses, it is entirely likely that both types of particles are responsible for the appearance of color. In this connection the instability of the color of copper rubies could be due to the presence of two color carriers, whose character of coloring is different and which require different approaches to the factors that give self-organization of nanoparticles (glass composition, glassmaking regime, extraction, “setting”).

**Color Setting of Colloidally Colored Glasses.** An important technological operation to obtain colloidally colored glass is “setting” the required color. In practice setting is accomplished using one of the following methods [7, 21 – 23]:

- simultaneously with extraction of the articles, for which the shaped article is briefly heated to obtain the required color;
- simultaneously with firing articles; in this case the articles are fired without color setting; color appears during firing;
- performing the special additional process of setting the color of articles or glass blanks (“hoses,” glass tubes, disks, and so on).

The choice of setting method depends on the type glass, method of formation, temperature interval, and setting time. A third setting method is usually used to obtain high-quality blown articles using a cover layer of gold ruby.

For photosensitive glass, setting can mean the action of external radiation, for example, ultraviolet radiation. The “setting” regimes in this case are determined by the glass composition, intensity, and exposure time of the radiation for the glass.

The appearance in recent years of an enormous interest in the colloidal state of matter under the trademark “nanotechnology” is due to its unique properties, the creation and development of technological processes and equipment (predominately in the field of microelectronics), and high-resolution monitoring-measurement equipment (scanning, tunneling, atomic-force, ionic-field microscopes and others) [5, 36].

It should be noted that nanotechnologies are still not used for purposeful and large-scale solutions of theoretical and practical problems of glasswork. At the same time analysis of the existing nanoeffects shows that the scales of the theoretical and experimental work in the field of nanostructures and the purposeful application of such structures

**TABLE 2.** Effect of the CdS and CdSe ratio on the Color of Cadmium and Sulfide and Sulfoselenide Colored Glass

Glass color	Ratio, %		Wavelength of absorption band edge, nm	$\Delta E$ , eV
	CdS	CdSe		
Yellow	100 (100)	0 (0)	470	CdS — 2.42 CdSe — 1.74
Orange	75 (65)	25 (35)	550	
Red	40 (40)	60 (60)	620	
Dark red	10 (15)	90 (85)	700	

**Note.** The numbers in parentheses are the CdS and CdSe content according to the data of [25].

must be increased in order to improve the effectiveness of the technology and the operational reliability of glass articles.

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